

Impregnated salts, their production and their use

The present invention relates to impregnated salts comprising at
5 least one salt of one or more carboxylic acids, which salt has
been impregnated with from 0.5 to 30% by weight, based on the
carboxylic acid salt, of at least one carboxylic acid, and to
preservatives comprising an impregnated salt and, where
appropriate, at least one carrier and/or formulation auxiliaries,
10 it being possible for the preservatives to be coated with a
protective agent and/or a dusting powder.

The invention furthermore relates to a process for producing the
impregnated salts and the preservatives, and to the use of the
15 salts and preservatives for the treatment of human and animal
food, and for use in silage.

Short-chain organic acids such as formic acid, acetic acid or
propionic acid are used for acidifying and preserving human and
20 animal food. Disadvantages of these acids are, for example, their
liquid state of aggregation at room temperature, the sharp or
pungent odor resulting from the low vapor pressure, and their
corrosiveness.

25 In addition, the liquid organic acids can be incorporated in
concentrated form, for example into animal food, only with
considerable technical complexity.

DE 28 33 727 A1 discloses a particulate fungicidal material which
30 comprises propionic acid and a carrier material. It is said that
with this material there is no increase in the number of mold
colonies on stored agricultural harvest products even after
incubation for several days. However, it has emerged that
material of this type is itself not stable on storage (loss of
35 acid), and the maximum amount of propionic acid which can be
applied depends greatly on the carrier material used. In
addition, unpleasant odors arise with this material owing to
evaporation of the propionic acid.

40 EP-A-0 590 856 and EP-A-0 608 975 disclose mixtures of solid
carboxylic acid salts and solid carboxylic acids with a lower pKa
than the carboxylic acid in the salts used. When this mixture is
dissolved in water, the carboxylic acids are liberated from the
salts by the carboxylic acid with the lower pKa in a displacement
45 reaction. The resulting new salts with the carboxylic acid with
the lower pKa are advantageously insoluble in water and
precipitate from the solution. A disadvantage of these mixtures

is that it is still necessary to use various carboxylic acids with different pKa values for producing the preservatives. In order to ensure that the carboxylic acids are completely liberated from the initial carboxylic acid salts (for example
5 from calcium propionate) on dissolving in water, the carboxylic acids with the lower pKa (for example maleic acid) must be added in at least equimolar amounts based on the carboxyl groups present in the acids. This limits the individual carboxylic acid active substance content. If insoluble carboxylic acid salts are
10 formed in this liberation, they must additionally be removed in a subsequent reaction.

It is an object of the present invention to provide novel compositions for treating human and animal food which do not have
15 the abovementioned disadvantages and can easily be mixed by the user without difficulty into the human and animal food to be treated. The main aim was to produce a solid composition which has a maximum active substance content and displays very little odor, if any. The solid final product should have good storage,
20 flow and processing properties.

We have found that this object is achieved by the novel impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5
25 to 30% by weight, based on the carboxylic acid salt, of at least one liquid carboxylic acid.

The invention additionally relates to preservatives comprising an impregnated salt of the abovementioned composition. In addition,
30 the preservatives may advantageously comprise at least one carrier and/or formulation auxiliary and, where appropriate, be coated with a protective agent and/or dusting powder.

The invention furthermore relates to a process for producing the
35 impregnated salts, which comprises impregnating at least one salt of a carboxylic acid or of a mixture of carboxylic acids with at least one liquid carboxylic acid until the concentration is 30% by weight based on the carboxylic acid salt.

40 The invention additionally relates to the production of preservatives comprising an impregnated salt of the abovementioned composition, which comprises impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight of
45 at least one liquid carboxylic acid being mixed where appropriate with at least one carrier and/or at least one formulation auxiliary, and being agglomerated with or without addition of one

or more binders, and subsequently the preservatives advantageously being provided with a protective agent which solidifies at room temperature (23°C), the protective agent being added in an amount such that the resulting preservatives are
5 coated and, where appropriate, further odorization is effected by, for example, adding fragrances. The preservatives produced in this way may advantageously also be coated with a finely dispersed dusting powder to improve the flow properties of the preservatives.

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The novel impregnated salts or preservatives have the advantage that the highly pungent odor of the acid is reduced. The impregnated salts advantageously comprise an active substance content of from 68 to 75% by weight, preferably 70 to 73% by
15 weight, particularly preferably 70 to 72% by weight, as total based on the total amount of carboxylic acids present in the salt and added. Both the novel impregnated salts and the preservatives release the acid content efficiently and rapidly from the solid and have good storage, flow and processing properties.

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Liquid organic acids suitable for impregnating the carboxylic acid salts are acids or mixtures of acids which are liquid or become liquid at the processing temperatures, preferably down to 40°C or below.

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C₁-C₈-mono- and/or dicarboxylic acids and the salts of these C₁-C₈-mono- and/or dicarboxylic acids are advantageously used to produce the impregnated salts or to produce the preservatives. Alkali metal, alkaline earth metal or ammonium salts are

30 suitable. Acids such as formic, acetic and/or propionic acid and their ammonium, calcium, lithium, sodium, magnesium and/or potassium salts are preferably used. The calcium, sodium or ammonium salts are advantageously used. However, also suitable in principle are other acids such as amino acids, hydroxy carboxylic
35 acids, oxo acids or mineral acids such as HCl or H₂SO₄ and their salts, with mineral acids being less preferred. It is possible to use single salts or mixtures of different salts of one carboxylic acid or several carboxylic acids which have been impregnated with one or more acids to produce the impregnated salts. The

40 impregnated salts advantageously consist of the salts of a carboxylic acid which have been impregnated with the same carboxylic acid. The impregnated salts preferably consist of the salt of a carboxylic acid which has been impregnated with the same carboxylic acid. Salts of formic acid and/or propionic acid
45 which have been impregnated with formic acid and/or propionic acid in a form which is as concentrated as possible, for example with 99% strength formic acid, are particularly preferred.

Impregnated salts produced from formic acid and the salts of formic acid are very particularly preferred.

X-Ray structural analysis of the novel impregnated salts shows an additional band by comparison with normal carboxylic acid salts.

The impregnated salts can, to improve handling, advantageously be mixed with other substances, for example with a carrier, and/or be dusted with a dusting powder.

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The term impregnation means applying at least one carboxylic acid, which is liquid at 40°C or below, to the solid carboxylic acid salt(s) so that the liquid carboxylic acid(s) penetrate(s) into the salt crystal(s). As a rule, this takes place with slight evolution of heat. For the impregnation, at least one carboxylic acid is applied in an amount of up to 30% by weight, based on the carboxylic acid salt(s), onto the salt(s), preferably applying the carboxylic acid(s) in an amount of from 0.5 to 30% by weight, particularly preferably applying from 15 to 25% by weight, very particularly preferably applying from 15 to 20% by weight, based on the salt component, to produce a solid substance as reaction product. With more than 30% by weight of acid, the salt crystals start to stick together; under these conditions, free carboxylic acid is present to some extent in addition to the impregnated salts. These crystals which are stuck together can be separated from one another by adding a release agent, and the free carboxylic acid can be taken up by the release agent. With more than 35% by weight of acid, the products stick together so strongly that a pasty texture results as a consequence of the free carboxylic acid. These pasty textures can be processed to granules for example in another working step by addition of a release agent and treatment in, for example, a mixer. Since further working steps and larger amounts of a release agent are necessary if more than 30% by weight of free acid is added, these embodiments are less preferred for economic reasons. However, it is possible in principle to improve the flow properties of the impregnated salts by adding small amounts of a release agent even with less than 30% by weight of carboxylic acid. Examples of suitable and advantageous release agents are Sipernats, Aerosils and/or Tixosils.

Thus, in the novel process for producing the impregnated salts, at least one salt of a carboxylic acid or of a mixture of carboxylic acids is impregnated with at least one carboxylic acid which is liquid at 40°C or below until the concentration is 30% by weight based on the carboxylic acid salt(s).

It is also possible in the novel process for producing the impregnated salts to add at least one salt of one or more carboxylic acids to at least one carboxylic acid. This mode of production is less favorable than addition to the salt(s) so that
5 under these conditions, for example when a mixer is used for production, an increased energy input is necessary.

The novel process for producing impregnated salts is advantageously carried out at a temperature determined by the
10 solidification point of the carboxylic acid used. The process is carried out at from 0 to 60°C, preferably from 15 to 50°C, particularly preferably from 20 to 40°C.

In a preferred embodiment, the novel salt also has a protective
15 agent and/or dusting powder on the surface of the crystals. The size of the impregnated salt crystals is preferably below 2.5 mm, particularly preferably from 10 μm to 2000 μm , very particularly preferably from 300 μm to 1500 μm .

20 The novel preservatives mean preservatives comprising impregnated salts which comprise at least one salt of one or more carboxylic acids and have been impregnated with at least one liquid carboxylic acid. These impregnated salts can be mixed in the preservatives with one or more carriers and/or formulation
25 auxiliaries. It is possible in the novel process for producing the preservatives to agglomerate this mixture with or without addition of binder. It is then possible to apply to these preservatives a protective agent which is soluble or swellable in water at 20°C and/or a finely dispersed dusting powder so that the
30 novel preservatives have a coating of a protective agent and/or dusting powder.

Carriers which can be employed are porous, organic or inorganic carrier materials whose particle sizes are from 1 μm to 1,000 μm ,
35 preferably from 5 μm to 100 μm .

Suitable in principle for producing such free-flowing, reduced odor agglomerates are all known organic or inorganic porous carriers as long as they are resistant to acid. Examples are
40 cereal brans, perlite, clay materials, silicates and silicas, with inorganic carriers being preferred because their properties can be controlled better.

Examples of other carriers which can be used are diatomaceous
45 earth, crushed sand, clay, nylon powder, insoluble metal oxides or insoluble metal salts, Aerosil, corundum, ground glass, granite, quartz or flint, aluminum phosphate, kaolin, bentonite,

zeolites, calcium silicate, talc, titanium oxide, active carbon or bonemeal.

Carriers which are preferably used are cereal brans, silicates,
5 perlite or silicas in amounts of from 10% to 70%, preferably 20 to 40%, of the weight of the impregnated salt.

Suitable binders in the novel process are water and/or synthetic or natural polymers, for example albumin, casein, soybean
10 protein, starch, synthetic cellulose derivatives such as carboxymethylcellulose, methylcellulose, hydroxymethyl-, hydroxyethyl- and/or -propylcellulose, polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone, gelatin, carrageenan, chitosan, dextrin, alginates, agar-agar, gum arabic, tragacanth
15 or guar gum, or mixtures thereof.

Protective agents which can be used are water-soluble polymers such as synthetic or natural polymers, for example gelatin, carrageenan, alginates or polyvinyl pyrrolidone, organic acids,
20 their salts or low-melting inorganic salts.

Protective agents which are preferably used are polyethylene glycols, polyvinylpyrrolidones or C_3 - C_{14} , preferably C_3 - C_6 , organic acids and their salts, in particular citric acid, fumaric
25 acid, succinic acid, adipic acid, benzoic acid and their salts, or amino acids and their salts.

In a preferred embodiment of the novel process for producing the preservatives, the carboxylic acid salt is introduced into a
30 mixer, impregnated with the organic acid, a carrier is admixed where appropriate, and subsequently agglomeration and coating with the protective agent are carried out in the presence or absence of a binder.

35 The impregnated salts and/or carrier particles are mixed with the protective agent, the latter ordinarily consisting of a highly concentrated solution or melt of substances which are soluble or swellable in water and solidify at room temperature (23°C). This protective agent is preferably applied in the heated state to the
40 impregnated salt and/or carrier particles and mixed with the latter. During this, the protective agent solidifies on the surface of the impregnated salts and/or carrier particles. Suitable mixer operating parameters result in agglomeration of different particles to larger granules.

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The size of the granules can be adjusted by processing parameters, for example during the mixing or during the fluidized

bed granulation, and by the amount and type of binder or else by subsequent screening or grinding. The granules preferably have an average diameter of less than 3 mm, in particular of 0.3 - 1.3 mm. It is possible where appropriate for residual water to be present in the protective agent used for coating and agglomeration. After the agglomeration process or directly after production of the impregnated salts, residual water can be bound by a dusting process with a dry and finely dispersed dusting powder. It is possible by this dusting process also to prevent the agglomerates or impregnated salts sticking together later and, in addition, to apply, for example, the salt of the organic acid used (eg. sodium or calcium formate or propionate) to the agglomerate or the salts. It is furthermore possible where appropriate to add a fragrance or flavoring, eg. vanillin, tecu flavor, citral or fructin, which makes it possible to achieve an additional odor-masking effect which, for example, makes the food attractive for animals to consume.

Protective agents which are preferably employed, such as binder liquids, are substances which are soluble or swellable in water and which solidify at room temperature. This makes it possible to dispense with a subsequent drying step in which, apart from a solvent or the additional water, part of the organic acid would also evaporate.

Particularly suitable protective agents for the agglomeration process and the coating are those which have a softening temperature above 30°C, preferably above 60°C, in order to avoid deformation of the agglomerates if the storage temperature is relatively high. The protective agents which are preferably used additionally do not counteract the pH-lowering effect of the adsorbed organic acid or even, where appropriate, assist or enhance the latter.

Examples of suitable protective agents are highly concentrated, hot sugar solutions or alkali metal/alkaline earth metal formate/acetate/propionate solutions. The residual water content thereof can be taken up by the final dusting step. Low-melting polyethylene glycols such as PEG 4000, melts of citric acid, of adipic acid, fumaric acid or benzoic acid or their salts, highly concentrated solutions of amino acids or mixtures of these acids are suitable and preferred as binder liquids. The amount of binder liquid used is from 0.5 to 80%, preferably 10 to 25%, but particularly preferably 5 to 15%, of the weight of the granules.

Suitable dusting powders are, besides the porous carrier materials themselves, finely disperse, ground organic acids or

their salts, eg. sodium formate, and inorganic salts, Sipernats, Tixosils or Aerosils. The amounts of dusting powders added are 10%, preferably from 0.1 to 5% by weight.

- 5 In general, at least one salt of one or more organic acids is introduced into a mixer, eg. an Eirich mixer, and impregnated with at least one organic acid with low energy inputs. However, the process can also be such that the liquid is introduced into the mixer, and the salts of the carboxylic acids are metered in.
- 10 Higher energy inputs are necessary in the latter case.

- Care must be taken to ensure uniform impregnation and to avoid excessive local moistening, which leads to lump formation. After the impregnation, the mixer contains a free-flowing carboxylic
- 15 acid salt in the form of a crystalline solid. The viscosity of the binder liquid which is subsequently metered in where appropriate should be adjusted, by appropriate selection of the temperature, so that it is below 1000 mPas, preferably < 100 mPas, in order to achieve a fine drop size distribution in
- 20 the spraying. In this preferred embodiment, owing to the temperature difference between the hot binder liquid and cooler impregnated salt, the drops of binder liquid initially solidify rapidly. As the agglomeration process progresses, the temperature of the bed increases owing to the mechanical and thermal energy
- 25 input by from 10 to 30°C, depending on the nature of the binder liquid. Further drops of binder liquid become attached to the previously formed agglomerates, and some of them coalesce together. The energy input increases during the agglomeration.
- 30 It is possible finally to add an odorizing agent along with the dusting powder as described above. Suitable for this in principle are a large number of fragrances and flavorings which can be selected depending on the subsequent use of the agglomerate. The content of these fragrances can be < 1%, preferably from 0.05 to
- 35 0.5%, of the weight of the granules. The agglomerates produced in this way contain little dust and have a reduced odor, and their organic acid content is readily soluble in water.

- The novel impregnated salts and/or preservatives are suitable for
- 40 acid treatment and/or preservation of human and animal foods, for use in silage or for leather treatment. Human and animal foods mean, in particular, grass, agricultural crops and/or compounded animal food and the materials used to produce them, such as hay, barley, wheat, oats, rye, corn, rice, soybeans, sugarcane
- 45 residues, sugarcane, rapeseed, peanuts, sunflower seeds, buckwheat chaff, silage, wet grains, pulse or grain crops, but also milk replacer, liquid, compound and mineral feeds, fish

silage or fish, meat or bone meal.

The novel preservatives may also contain other additives such as minerals, vitamins, antibiotics or protein additives. The

- 5 preservatives may, in particular, contain other additives with fungicidal or bactericidal properties, such as formalin, formic acid, acetic acid, propionic acid, benzoic acid, sorbic acid or bisulfites.

- 10 The novel impregnated salts and/or preservatives are advantageously added to the material to be preserved in an amount of, in each case, from 0.1 kg to 25 kg, preferably from 0.5 kg to 20 kg, particularly preferably from 5 to 15 kg, per ton of material to be preserved.

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Examples

(Purity of the formic acid and propionic acid used = 99%)

20 A. Formic acid

Example 1

- 25 100 g of sodium formate were introduced into a household mixer (Braun), and 15% by weight of formic acid were added. The temperature rose from 22°C to 40°C on uptake of the acid. The resulting product (= impregnated salt) was free-flowing and odorless.

30 Example 2

- 35 100 g of calcium formate were introduced into a household mixer, and 15% by weight of formic acid were added. The resulting product had a slightly pungent odor of formic acid and showed cohesive behavior, ie. the resulting impregnated salt was slightly damp and not free-flowing.

Example 3

- 40 100 g of potassium formate were introduced into a household mixer, and 10% by weight of formic acid were added. The temperature rose from 23°C to 45°C on uptake of the acid. The impregnated salt had a slightly pungent odor and showed a slight tendency to become granular.

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B. Propionic acid

Example 4

- 5 100 g of fumaric acid were introduced into a household mixer, and 15% by weight of propionic acid were added. The product was highly cohesive and had an intense odor.

Example 5

- 10 100 g of sodium formate were introduced into a household mixer, and 15% by weight of propionic acid were added as in the previous examples. The product is highly cohesive and has an intense odor.

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Example 6

- 20 100 g of calcium formate were introduced into a household mixer, and 15% by weight of propionic acid were added. The temperature rose slightly while the acid was taken up. The product had an intense odor and showed a cohesive behavior.

Example 7

- 25 100 g of calcium propionate were introduced into a household mixer, and 15% by weight of propionic acid were added. The temperature rose from 23°C to 29°C on uptake of the acid. The product is free-flowing and has an intense odor.

30 C. Production of preservatives

Example 8

- 35 1000 g of sodium formate were introduced into an Eirich mixer (RO2) and impregnated with 15% by weight of formic acid. 200 g of sodium formate melt at 80°C are sprayed as binder from a heated storage container through a two-component nozzle onto 1000 g of this mixture into the mixing chamber. The resulting agglomerates are dusted with 44 g of Sipernat®
- 40 (= highly disperse silica supplied by Degussa). The resulting product is free-flowing and odorless.

Example 9

- 45 1000 g of sodium formate were introduced into an Eirich mixer and impregnated with 15% by weight of formic acid. For agglomeration and coating, 180 g of a concentrated glucose

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solution at 80°C are sprayed as binder from a heated storage container through a two-component nozzle into the mixing chamber. The resulting agglomerates are dusted with 45 g of Sipernat® and 12 g of citral. The acid content is then 59.5%.
5 The resulting agglomerates are free-flowing.

Example 10

10 As in Example 9, 500 g of sodium formate were introduced into an Eirich mixer and impregnated with 15% by weight of formic acid. Then 500 g of perlite were added. 260 g of citric acid melt at 170°C are sprayed in as binder from a heated storage container through a two-component nozzle into the mixing
15 chamber. The resulting agglomerates are dusted with 44 g of Sipernat® and 8 g of vanillin. The total acid content is 29.7%. The resulting preservatives are free-flowing and odorless. The impregnated salts described in Examples 1 to 7 can also be converted as in Examples 8 to 10 into free-flowing preservatives with a reduced odor or no odor.

20 The following Examples 11 to 14 show storage stability tests for an impregnated salt (sodium formate impregnated with 20% by weight formic acid) treated with various protective agents and/or dusting powders (see Table 1). Part-quantities of the
25 impregnated salts were placed in a tumbler mixer and mixed for a further 10 min while adding the additives (see Table 1). The products were then introduced into a steel vessel (diameter about 40 mm) up to 15 - 20 mm below the rim of the vessel and stored in a drying oven at 35°C under load
30 (simulated with a metal piston), the load corresponding to simulated storage under normal storage conditions, and tested at the stated times. Because of the small diameter of the test vessel and the storage under pressure, in order to
35 establish whether a product is free-flowing or not, it is necessary to tap the vessel. The terms used to indicate the result of the flow test have the following meanings:
gentle tapping 1x, gentle tapping 2x and tapping 1x = product is free-flowing
tapping 3x = product shows caking but is essentially
40 free-flowing
tapping 4x, tapping 5x and tapping >5x = product is caked and essentially no longer free flowing.

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Table 1: Storage stability of the impregnated salts

Exam- ple	Storage time in days	Additive	Flow test	Remarks
11	7 d	1% FK500LS ¹	tapping 1x	slightly caked, loose
		2% FK500LS	tapping 1x	no caking
		4% FK500LS	gentle tapping 1x	no caking
		1% Sip.50S ²	gentle tapping 2x	caked
		2% Sip.50S	gentle tapping 1x	no caking, dust
		4% Sip.50S	gentle tapping 1x	no caking, dust
12	14 d	1% Aero- sil200 ³	tapping 3x	caked
		2% Aero- sil200	tapping 2x	slightly caked
		3% Aero- sil200	tapping 1x	no caking
		4% Aero- sil200	-	
		5% Aero- sil200	tapping 2x	no caking, dust
		2% Aero- sil200 + 2% D17 ⁴	tapping 2x	no caking, much dust
		2% D17	tapping 1x	slight caking, dust
		5% D17	tapping 1x	no caking, dust

	Exam- ple	Storage time in days	Additive	Flow test	Remarks
5	13	7 d	2% R972 ⁵ + 2% benzoic acid	tapping >5x	very caked
			2% R972 + 2% Na benzoate	tapping >5x	very caked
10			2% R972 + 2% K sorbate	tapping >5x	very caked
			4% R972	tapping 4x	caked
			2% R972 + 1% FK500LS	tapping 1x	no lumps
15			2% R972 + 2% FK500LS	tapping 1x	dust, no lumps
			2% R972 + 2% Zeolite ⁶	tapping 5x	very caked
20			2% R972 + 2% sorbitol	tapping >5x	very caked
	14	7	1% Aerosil200	tapping 3x	caked
25			2% Aero- sil200	tapping 2x	slightly caked
			3% Aero- sil200	tapping 1x	slightly caked
			4% Aero- sil200	tapping 3x	not caked, dust
30			5% Aero- sil200	tapping 3x	not caked, dust
			2% cornmeal	tapping >5x	very caked
			5% cornmeal	tapping >5x	very caked
35			2% D17	tapping 1x	slightly caked
			2% D17	tapping 1x	not caked, dust
			1% Aero- sil200 + 2% R972	tapping 1x	not caked
40			2% Aero- sil200 + 2% R972	tapping 1x	slightly caked, dust

1,2,3,4,5 various silicas supplied by Degussa

45 ⁶ Zeolite supplied by Degussa

D. Acidification of foodstuffs

Example 15

5 A piglet starter feed was treated with 10 kg/t or 20 kg/t of
an impregnated salt (sodium formate/15% by weight formic
acid). The pH of the feed fell from 6.4 to respectively 5.5
or 5.1.

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